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4-Methyl-2-(2-methylanilino)benzoic acid

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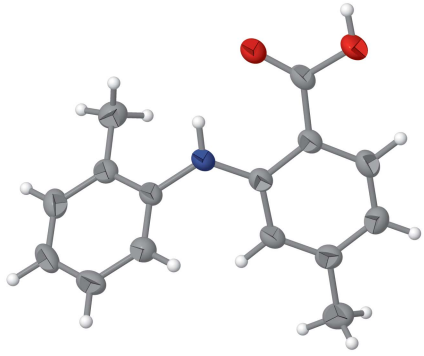
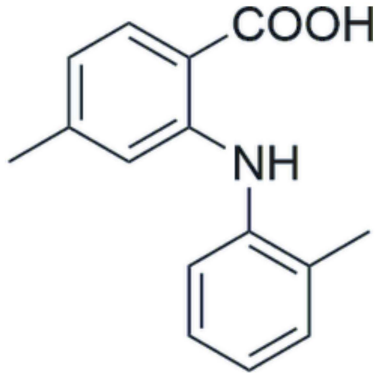
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{15}H_{15}NO_2$, was obtained by the reaction of 2-chloro-4-methyl-benzoic acid and *o*-toluidine using 2-ethoxyethanol as solvent. Crystals of the title compounds were obtained from crystallization in acetone. The molecule in the crystal is twisted with a dihedral angle between the aromatic rings of 50.86 (5)°. In the crystal structure, the molecules associate to form acid–acid hydrogen-bonded dimers linked by pairwise O—H···O hydrogen bonds.

3D view



Chemical scheme



Structure description

Anthranilic acids are compounds with great medicinal value. They play an important role in non-steroidal anti-inflammatory (Masubuchi *et al.*, 1998), antibacterial (Abdulkarem *et al.*, 2019) and antiviral agents (Inglot 1969) and other drugs. The title compound has a methyl group on both aromatic rings (Fig. 1). As a result of steric repulsion, the aromatic rings are not coplanar with a dihedral angle of 50.86 (5)°. In the crystal, two molecules pair up to form a carboxylic acid–carboxylic acid hydrogen-bonded dimer. An intramolecular N1—H1*A*···O2 hydrogen bond (Table 1, Fig. 2) is also observed.

Synthesis and crystallization

The title compound was prepared by reacting 2-chloro-4-methyl-benzoic acid and *o*-toluidine in the presence of a catalyst at 403 K (Fig. 3). The product was purified by column chromatography. Single crystals were obtained by slowly evaporating an acetone solution of the compound (Fig. 4).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

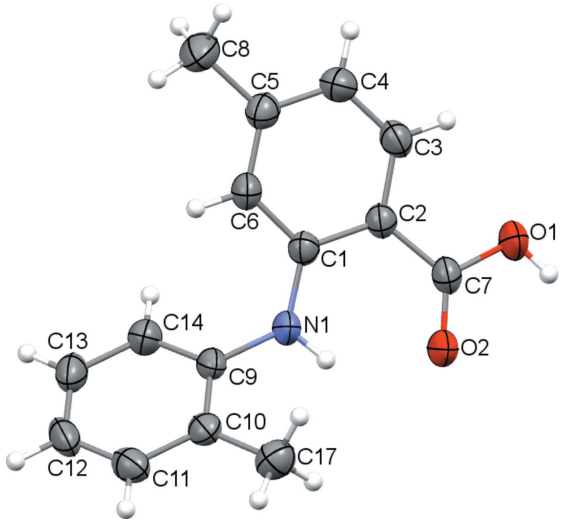


Figure 1
Molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level.

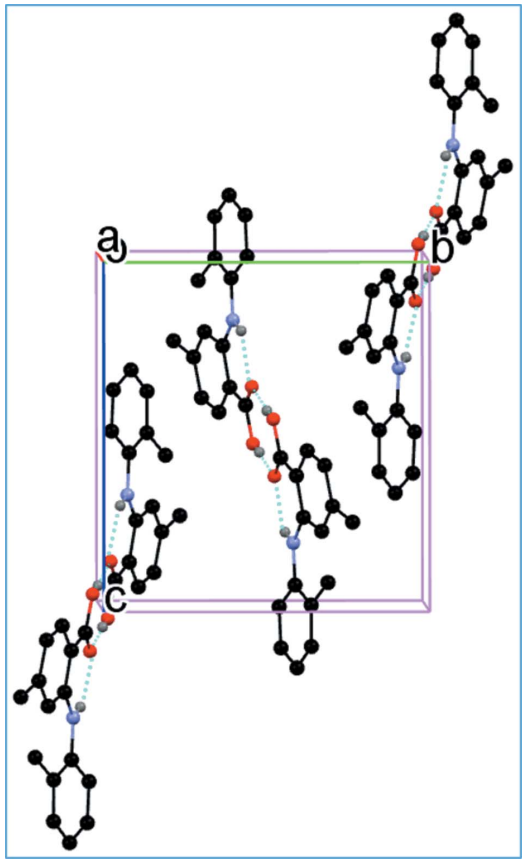


Figure 2
Packing of the molecules in the title compound (for clarity, H atoms not involved in hydrogen bonding are omitted). Hydrogen bonds are indicated by dashed lines.

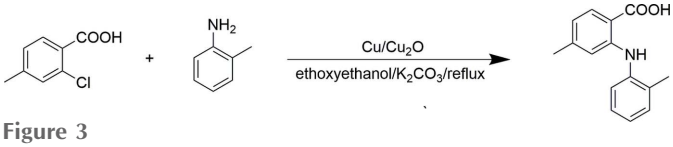


Figure 3
Reaction scheme.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^{i}	0.82	1.84	2.6570 (17)	174
N1—H1A···O2	0.86	2.01	2.6942 (17)	136

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{15}H_{15}NO_2$
M_r	241.28
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	9.6678 (8), 10.9294 (11), 11.7231 (8)
β (°)	93.395 (7)
V (Å^3)	1236.53 (18)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.69
Crystal size (mm)	0.08 × 0.04 × 0.02
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Eos
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.919, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4437, 2285, 1828
R_{int}	0.019
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.609
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.131, 1.04
No. of reflections	2285
No. of parameters	166
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.25, −0.20

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXS* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2020).

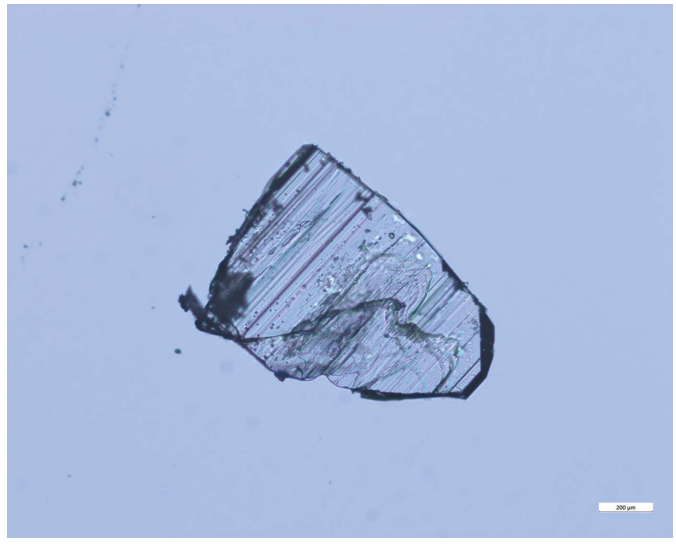


Figure 4
A representative crystal of the title compound.

Funding information

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full crystallographic data

IUCrData (2023). **8**, x230599 [https://doi.org/10.1107/S2414314623005990]

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Crystal data

$C_{15}H_{15}NO_2$
M_r = 241.28
Monoclinic, $P2_1/c$
a = 9.6678 (8) Å
b = 10.9294 (11) Å
c = 11.7231 (8) Å
β = 93.395 (7)°
V = 1236.53 (18) Å^3
Z = 4
$F(000)$ = 512
D_x = 1.296 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 1387 reflections
θ = 9.3–69.0°
μ = 0.69 mm^{-1}
T = 293 K
Plate, clear light colourless
0.08 × 0.04 × 0.02 mm

Data collection

SuperNova, Dual, Cu at zero, Eos diffractometer
Radiation source: micro-focus sealed X-ray tube, SuperNova (Cu) X-ray Source
Mirror monochromator
Detector resolution: 16.0733 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2015)
T_{min} = 0.919, T_{max} = 1.000
4437 measured reflections
2285 independent reflections
1828 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 70.0°, θ_{min} = 4.6°
h = −11→11
k = −12→13
l = −13→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.131
S = 1.04
2285 reflections
166 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0678P)^2 + 0.2398P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. The positions of H atoms in N1 and O1 were obtained from the difference Fourier map. Other H atoms were positioned geometrically with C—H = 0.93 for aromatic, and constrained to ride on their parent atoms with U_{iso}(H) = xU_{eq}(C,*O*), where *x*=1.5 for all H atoms.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.32010 (13)	0.52719 (14)	0.45925 (9)	0.0527 (4)
H1	0.396573	0.509295	0.437474	0.079*
O2	0.44087 (12)	0.53328 (13)	0.62639 (9)	0.0487 (4)
N1	0.30228 (14)	0.58797 (15)	0.81250 (11)	0.0434 (4)
H1A	0.377666	0.564178	0.783957	0.052*
C1	0.19420 (15)	0.61667 (15)	0.73583 (13)	0.0332 (4)
C2	0.20410 (16)	0.59559 (14)	0.61709 (13)	0.0333 (4)
C3	0.09126 (17)	0.62616 (17)	0.54234 (13)	0.0409 (4)
H3	0.096893	0.611557	0.464602	0.049*
C4	−0.02712 (18)	0.67684 (17)	0.57997 (15)	0.0455 (4)
H4	−0.100826	0.695348	0.528272	0.055*
C5	−0.03698 (17)	0.70070 (16)	0.69615 (15)	0.0405 (4)
C6	0.07217 (16)	0.66986 (16)	0.77176 (13)	0.0375 (4)
H6	0.064581	0.684862	0.849231	0.045*
C7	0.33051 (17)	0.54979 (15)	0.57000 (13)	0.0365 (4)
C8	−0.1651 (2)	0.7593 (2)	0.73824 (18)	0.0614 (6)
H8A	−0.238018	0.699747	0.739025	0.092*
H8B	−0.193583	0.825546	0.688383	0.092*
H8C	−0.145628	0.790187	0.814164	0.092*
C9	0.30353 (16)	0.59315 (16)	0.93298 (13)	0.0357 (4)
C10	0.41723 (16)	0.64529 (16)	0.99389 (13)	0.0370 (4)
C11	0.41862 (18)	0.64593 (17)	1.11262 (14)	0.0452 (4)
H11	0.494677	0.678781	1.154221	0.054*
C12	0.3104 (2)	0.59922 (19)	1.17011 (14)	0.0492 (5)
H12	0.312562	0.602599	1.249460	0.059*
C13	0.19886 (19)	0.54745 (18)	1.10961 (15)	0.0475 (5)
H13	0.125187	0.516229	1.148058	0.057*
C14	0.19640 (18)	0.54187 (17)	0.99152 (14)	0.0426 (4)
H14	0.122853	0.503693	0.951043	0.051*
C17	0.53483 (18)	0.69949 (18)	0.93333 (16)	0.0495 (5)
H17A	0.582818	0.635765	0.895481	0.074*
H17B	0.597691	0.739472	0.987773	0.074*
H17C	0.499370	0.757976	0.877931	0.074*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0452 (7)	0.0860 (11)	0.0276 (6)	0.0073 (7)	0.0069 (5)	−0.0103 (6)
O2	0.0421 (7)	0.0745 (9)	0.0299 (6)	0.0147 (6)	0.0058 (5)	−0.0046 (6)
N1	0.0337 (7)	0.0716 (11)	0.0253 (7)	0.0098 (7)	0.0055 (5)	−0.0038 (6)
C1	0.0326 (8)	0.0379 (8)	0.0294 (8)	−0.0023 (6)	0.0041 (6)	0.0010 (6)

C2	0.0350 (8)	0.0363 (8)	0.0288 (8)	−0.0023 (6)	0.0046 (6)	−0.0002 (6)
C3	0.0455 (9)	0.0493 (10)	0.0279 (8)	−0.0026 (8)	0.0019 (7)	0.0000 (7)
C4	0.0381 (9)	0.0576 (11)	0.0403 (9)	0.0025 (8)	−0.0021 (7)	0.0065 (8)
C5	0.0374 (9)	0.0438 (9)	0.0407 (9)	0.0020 (7)	0.0076 (7)	0.0061 (7)
C6	0.0388 (9)	0.0450 (9)	0.0295 (8)	0.0025 (7)	0.0082 (6)	0.0001 (7)
C7	0.0419 (9)	0.0422 (9)	0.0260 (7)	−0.0010 (7)	0.0066 (6)	−0.0007 (6)
C8	0.0493 (11)	0.0798 (15)	0.0563 (12)	0.0212 (11)	0.0120 (9)	0.0121 (11)
C9	0.0347 (8)	0.0457 (9)	0.0269 (7)	0.0108 (7)	0.0038 (6)	−0.0002 (7)
C10	0.0364 (8)	0.0400 (9)	0.0347 (8)	0.0094 (7)	0.0029 (6)	−0.0011 (7)
C11	0.0490 (10)	0.0497 (10)	0.0361 (9)	0.0095 (8)	−0.0051 (7)	−0.0046 (8)
C12	0.0610 (11)	0.0618 (12)	0.0251 (8)	0.0175 (9)	0.0044 (8)	0.0031 (8)
C13	0.0463 (10)	0.0587 (11)	0.0390 (9)	0.0109 (9)	0.0151 (8)	0.0124 (8)
C14	0.0363 (8)	0.0560 (11)	0.0358 (9)	0.0029 (8)	0.0046 (7)	0.0026 (8)
C17	0.0411 (9)	0.0543 (11)	0.0531 (11)	−0.0015 (8)	0.0036 (8)	0.0009 (9)

Geometric parameters (Å, º)

O1—C7	1.3196 (18)	C5—C6	1.379 (2)
O2—C7	1.235 (2)	C5—C8	1.504 (2)
N1—C1	1.374 (2)	C9—C10	1.396 (2)
N1—C9	1.4129 (19)	C9—C14	1.394 (2)
C1—C2	1.420 (2)	C10—C11	1.391 (2)
C1—C6	1.402 (2)	C10—C17	1.498 (2)
C2—C3	1.399 (2)	C11—C12	1.376 (3)
C2—C7	1.459 (2)	C12—C13	1.377 (3)
C3—C4	1.368 (2)	C13—C14	1.385 (2)
C4—C5	1.396 (2)		
C1—N1—C9	127.31 (13)	O1—C7—C2	114.81 (14)
N1—C1—C2	120.78 (14)	O2—C7—O1	120.84 (14)
N1—C1—C6	121.27 (14)	O2—C7—C2	124.35 (14)
C6—C1—C2	117.94 (14)	C10—C9—N1	119.17 (14)
C1—C2—C7	122.22 (14)	C14—C9—N1	120.90 (15)
C3—C2—C1	118.69 (14)	C14—C9—C10	119.86 (15)
C3—C2—C7	118.99 (14)	C9—C10—C17	121.04 (15)
C4—C3—C2	122.08 (15)	C11—C10—C9	118.32 (15)
C3—C4—C5	119.82 (15)	C11—C10—C17	120.64 (16)
C4—C5—C8	120.33 (16)	C12—C11—C10	121.71 (17)
C6—C5—C4	119.19 (15)	C11—C12—C13	119.69 (16)
C6—C5—C8	120.47 (16)	C12—C13—C14	119.98 (16)
C5—C6—C1	122.24 (15)	C13—C14—C9	120.36 (17)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^{i}	0.82	1.84	2.6570 (17)	174

N1—H1*A*···O2	0.86	2.01	2.6942 (17)	136

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.